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# High temperature materials for $CO_2$ capture

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**Abstract**

The potential benefits of precombustion carbon dioxide capture are well documented, and adsorption remains a promising separation process in this area. This paper details work to identify and assess the potential of high temperature adsorbents suitable for precombustion capture.

The aim of this paper is to schematically identify adsorbents that are suitable for carbon capture in different temperature ranges. A critical aspect of this work is to assess the materials not only in terms of carbon dioxide isotherms and absolute loading, but to consider the wide range of other properties that are required to achieve an industrially feasible adsorbent – selectivity, cycling capacity, stability, kinetics, high pressure loading, fate of other components (including water**,** $H_2S$, $NH_3$, CO and $N_2$). It is only when all these requirements are sufficiently met, that an adsorbent can be consider worthy of industrial consideration. A range of analytic screening tests are described to enable a full characterisation of the merit of a specific adsorbent.

The adsorbents investigated are zeolites (NaX, calcium chabazite), commercially available hydrotalcite, layered double hydroxides/oxides (LDH/Os), and magnesium double salts. Each operates in a different temperature range and offers potential for integration within an Integrated Gasification and Combined Cycle precombustion process train.

Some of the promising and significant conclusions of this work are –

- Magnesium double salts present very favourable carbon dioxide isotherms and demonstrate significant carbon dioxide loading and the isotherms are suitable for PSA or TSA operation at high temperature.
- LDHs or their derivatives as layered double oxides can adsorb up to 1.5mol/kg $CO_2$. Water does not affect $CO_2$ sorption, and the material has good recyclability in TSA.
- The selectivity of hydrotalcite is well documented. However there is no reported literature on the adsorptive behaviour of these materials with respect to trace components – $H_2S$ and $NH_3$. These results are reported.
- Calcium chabazite displays useful $CO_2$ loading potential in a unique temperature range around 200$^o$ C.
- NaX has the potential to replace Selexol at an operating temperate of 130$^o$ C.



*Keywords:* Type your keywords here, separated by semicolons ; IGCC; high temperature adsorbents; CO2 capture; PSA; TSA

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## 1. Introduction

There is considerable interest in identifying carbon dioxide capture processes that can be incorporated within Integrated Gasification and Combined Cycle (IGCC) systems. These so-called precombustion capture approaches offer a number of advantages over the end of stack post-combustion capture. The primary advantage of precombustion capture is significantly higher available carbon dioxide partial pressure. The essential argument is that while gasification processes have a higher capital cost than traditional pulverized coal, the overall cost of gasification with precombustion carbon dioxide capture is lower than pulverized coal with post-combustion capture. The incremental cost of capture is therefore expected to be lower for pre-combustion capture. There are also opportunities to integrate carbon dioxide capture within the water-gas shift reactor. This is a potentially important direction for Carbon Capture and Storage (CCS) research.

There are a number of different separation technologies that can be applied to precombustion carbon dioxide capture including solvent, membrane, and adsorbent based processes. The conventional approach is UOP's liquid absorption Selexol process which is one process option for the simultaneous removal of hydrogen sulphide and capture of carbon dioxide from the IGCC processes. However, one potential limitation of this process is that the liquid scrubbing must occur at relatively low temperatures (near ambient). This requires cooling of the gas exiting the Water Gas Shift reactor, capturing the carbon dioxide and hydrogen sulphide (acid gas removal), and then reheating the gas prior to the power block (gas turbine). These cooling and reheating steps add to the capital cost and reduce the efficiency of the power cycle [1]. By contrast, membrane and adsorbent based processes offer the potential of higher temperature capture eliminating the intermediate cooling and reheating steps. Recently these efforts have further focused on integrated membrane-Water Gas Shift reactor or Sorption Enhanced WGS that enable simultaneous hydrogen synthesis and carbon dioxide capture [2]. These are important research directions, however ultimately careful techno-economic assessment is required to compare the totality of these different capture strategies [3].

One important step in the development of high temperature carbon dioxide capture is the identification of potential adsorbents that could be utilised within an IGCC process train. The main difficulty with adsorbent selection for high temperature capture is that carbon dioxide loading capacity is only one of a number of necessary requirements for an effective adsorbent for high temperature capture. The aim of this paper is to outline the additional requirements and tests that we implemented to provide a fuller screening process to assist in the development of a high temperature adsorbent based carbon dioxide capture process. At this stage there is no claim that high temperature capture is the preferred process over existing solvent processes.

Rodrigues and co-workers have previously outlined a number of requirements for an effective high temperature adsorbent [4]. The requirements are: high adsorbent capacity, high selectivity, good mechanical strength, stable adsorption capacity after cycles, and adequate adsorption / desorption kinetics. This is a useful starting point to consider adsorbent properties beyond carbon dioxide loading capacity. However the list remains too generic. We need to more fully appreciate the operating environment of a carbon dioxide adsorbent between (or within) a Water Gas Shift reactor and a gas turbine.

From the IGCC process it is evident that a key requirement of the adsorbent is operation at elevated temperatures. The ideal temperature range is 250-450$^{\circ}$C for a separate carbon dioxide capture step or for integration within a WGS reactor. This operating temperature window is a significant challenge as was noted by Siriwardane et al., "there are no regenerable sorbents with sufficient carbon dioxide removal capacity at 250-350$^{o}$C reported in the literature" [5]. There are a range of materials that are suited for capture of carbon dioxide at higher and lower temperatures. For example, there are carbon based adsorbents and zeolitic materials that are suitable carbon capture to up ~120$^{\circ}$C . Additionally, there are also materials suited for carbon dioxide capture at more elevated temperatures ~ 500 -700$^{\circ}$C including lithium silicates, lithium zirconate and calcium and other metal oxides. Under some IGCC operating conditions it is possible to consider that carbon capture could occur at these higher temperature, however this is not viewed as the likely temperature range, particularly given the typical high temperature WGS reaction (450$^{\circ}$C).

In addition to the key requirement of a specific ideal temperature window there are a range of other essential requirements such as:

(1) high selectively for carbon dioxide over the other gases in a syngas mixture within the identified temperature range
(2) high adsorption working capacity for carbon dioxide within the identified temperature range
(3) adequate adsorption/desorption kinetics for carbon dioxide under operating conditions
(4) stable adsorption capacity for carbon dioxide after repeated adsorption/desorption cycles
(5) regenerability of adsorbent without extreme temperature and pressure conditions. Within the scope of this study, sorbents that can capture carbon dioxide to 500°C are of interest even where the regeneration temperature is higher
(6) adequate mechanical strength of adsorbent particles after cyclic exposure to high-pressure streams including high resistance to repeated stresses, e.g., expansion and shrinkage
(7) tolerance to the presence of water or impurities (such as hydrogen sulphide, ammonia, mercury, hydrogen chloride, water, carbon monoxide)
(8) low pressure drop
(9) a high thermal diffusion efficiency if TSA regeneration is pursued
(10) mechanical strength and ability to be formed into pellets or beads
(11) regeneration strategy and need to achieve carbon dioxide pressurisation to 100 bar for eventual transportation and storage.

There are a number of classes of adsorbents identified in the literature that exhibit some of above properties to a greater or lesser extent. The potential adsorbents identified can be divided into the following broad classes –

- Hydrotalcite based materials including Potassium Carbonate Promoted
- Alkali impregnated Alumina (including straight activated alumina)
- Double Salts
- LDH and LDO
- Carbonation Sorbent Reactions with Alkali Hydroxide and Alkali Oxides
- Zeolitic materials with carbon dioxide loading capacity at elevated temperatures ( ~ 250°C) (Chabazites) (While 13X retains $CO_2$ loading capacity at 120°C, and while not ideal this make prove acceptable within an IGCC process)

In this brief report we examine some of the requirements for these materials. The results reported in this paper are the initial phase of a research project (Energy Technology Innovation Strategy ETIS project) funded by the Victorian state government of Australia to demonstrate a precombustion carbon dioxide capture strategy to be integrated within an IGCC process. This work is ongoing and adsorbent screening is the initial phase. Subsequent testing will be carried out under actual IGCC conditions.

## 2. **Experimental :**

Materials: 13X beads were procured from UOP; $K_2CO_3$ promoted HTCs (MG Plural 70) were purchased from SASOL, Germany. LDH, Mg-Na double salts and K-Mg double salts as well as chabazite zeolite, were synthesized in the laboratory by known procedures [6, 7]. The Ca form of chabazite (CaCHA) was prepared by repeated ion-exchanges with 1M$CaCl_2$ solution at 60°C. Layer Doubled Oxide (LDO) were derived by the calcination of Mg–Al–$CO_3$ Layer Doubled Hydroxide (LDH) which was synthesised via the co-precipitation method of $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3$, $H_2O$ in a base solution containing NaOH and $Na_2CO_3$ as described elsewhere [8].

Analysis and characterization: Phase purity of the zeolites was determined by X-ray diffraction (Phillips), using Cuα radiation (λ = 1.5404 Å). The BET surface area of the samples was determined on an ASAP 2010 (Micromeritics) analysis using $N_2$ gas. High temperature adsorption isotherms for $CO_2$ (Linde gas) at 1 bar were measured on an ASAP 2020 using the chemisorption option (Micromeritics). Analysis of trace components such as $NH_3$ (1% in Helium, Coregas) and $H_2S$ (1% in Helium, Coregas) using Helium as protective gas and cyclic measurements for

$CO_2$ were performed using a TG/DTA analyzer (Mettlar-Toledo). All the samples were activated in the temperature range 300 to 400°C before measurement. Thermo gravimetric sorption of $CO_2$, $N_2$ and water on LDO was measured using a Shimadzu TG50 at 200°C.

**Results**

Table 1 displays the experimental results of $CO_2$ adsorption, selectivity and loading of trace components at 1 bar. The temperatures of adsorption varies with the sample, typically for zeolites the $CO_2$ adsorption was measured in the temperature range 90-250°C (medium range), while for hydrotalcites and LDH, temperatures greater than 350°C were used as these materials do not show significant adsorption below 350°C.

Table 1: Experimental results on different adsorbents, with different components at 1bar

| materials | Temp °C | $CO_2$ mol/kg | $CO_2/N_2$ Sel. | $H_2S$ mol/kg | $NH_3$ mol/kg | $H_2O$ mol/kg | Comments* |
|---|---|---|---|---|---|---|---|
| 13X | 120<br>200 | 2.62<br>0.67 | 29<br>- | 1.85<br>- | 4.0 [9]<br>- | 11.4<br>13.9 ‡ | $H_2S$: loads and unloads reversibly; $NH_3$: strongly loads (TSA required for regeneration); $H_2O$ loads, strong vacuum or heating required for desorption. |
| CaCHA | 120<br><br>200<br>400 | 2.79<br><br>1.09<br>0.61 | <br><br>27 | -<br><br>3.91 | -<br><br>0 | 16<br>(30°C)<br>TBA<br>- | $H_2O$: very difficult to unload (vacuum or heating required); $H_2S$: unloading difficult; CO loads slightly (reversible) |
| HTC | 300<br><br><br>400 | 0.20<br><br><br>0.46 | "High" [10]<br><br><br>"High" [10] | 1.79 | 0.02 | very low [10] | $H_2S$: regeneration difficult; $NH_3$: readily regenerated |
| Mg-Na DS† | 375 | 4.70 | "High" [6] | 1.74 | 0 | TBA | $H_2S$: unloading difficult |
| Mg-K DS | 375 | 1.5 | High [6] | 2.08 | 0 | TBA | |
| LDO | 200 | 1.2 | > 100 | | | 0.94 | Tests carried out with SOx in post combustion flue gases show that SOx preferentially sorbs on LDO [11] |

+ water data collection under actual precombustion conditions is to be undertaken.

* loading and unloading under partial pressure swing conditions.

† DS = double salts; reproducibility difficult.

‡Data from UOP: Water measured on 13 X , 1 bar water partial pressure

$CO_2$ adsorption capacity:

From Table 1, it is evident that zeolites are only effective $CO_2$ adsorbents in the temperature range 90 – 250°C. The optimum temperature for 13X is approximately 120°C beyond which it loses its capacity, while CaCHA zeolite retains its capacity up to 200°C (Figure 1). HTC's and Mg double salts operate in a high temperature range, and exhibit very high adsorption capacity and selectivity for $CO_2$. Mg double salts (Mg-NaDS) show a very unusual adsorption isotherm (Figure 2) and are extremely promising candidates for high temperature capture although we have encountered difficulty in producing reproducible samples. At 300°C, the sample shows excellent adsorption capacity which is however lost on repeated cycling and requires reactivation to 400°C. At 400°C adsorption is still

present but reduced. There appears to be a combination of chemisorption and physisorption leading to an "optimal" operating temperature which is approximately 375°C.

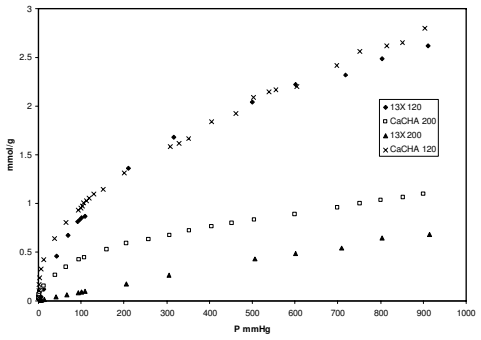


Figure 1. Adsorption of $CO_2$ on 13X and CaCHA

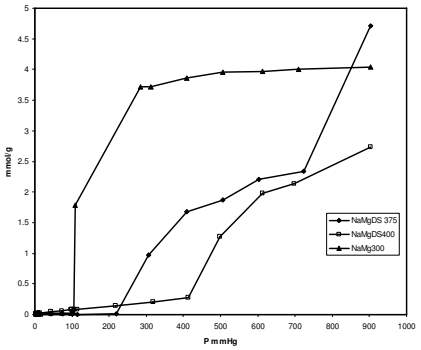


Figure 2. Adsorption of $CO_2$ on NaMG double salts

Water adsorption:
Zeolites 13X and CaCHA adsorb considerable amounts of water and in the absence of a thermal influence require very deep vacuum to regenerate the zeolite. In the presence of water, the $CO_2$ capacity is significantly reduced [13]. In the case of double salts, HTC's and LDO's, it does not appear that water influences their operation [8,10,12]. The treatment of water while capturing $CO_2$ is a major engineering issue which must be overcome before adsorption processes can play a role in $CO_2$ capture.

Ammonia and Hydrogen sulphide adsorption:
Zeolite 13X loads ammonia strongly at 120°C [9] and a TSA cycle is required for desorption. However, $H_2S$ loading appears to be reversible under the temperature conditions studied. We have studied the adsorption/desorption of $H_2S$ and $NH_3$ on CaCHA using a TGA and have observed the opposite behavior to 13X. Thus CaCHA strongly loads $H_2S$ at the temperatures studied (200°C), and does not load ammonia. TGA experiments using 1% H2S in Helium and 1% NH3 in helium were conducted on HTC materials. Figure 3 indicates the gravimetric results for $H_2S$ addition to HTC. Regeneration was attempted by physical purge (not thermal means) to see if it was possible to utilize a pressure wing adsorption cycle. As seen from Figure 3, $H_2S$ is strongly adsorbed to HTC and is not desorbed under purge regeneration. Thus thermal means will be needed to regenerate HTC if it is to be utilized in IGCC conditions. We have repeated these tests for double salts (not shown) and observed that $H_2S$ is adsorbed but not desorbed under purge regeneration.

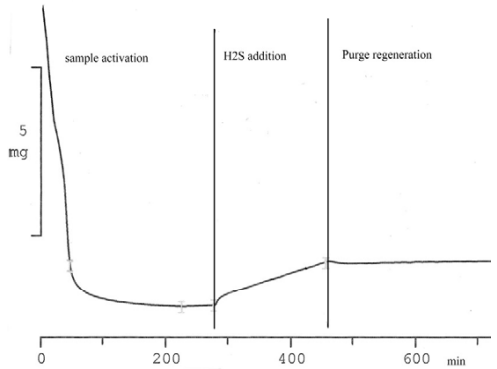


Figure 3. TGA Results from $H_2S$ addition to HTC

Cycling Requirements

A range of cycling experiments of $CO_2$ and impurities on the adsorbents was carried out on our TGA. There are two requirements for cycling capacity: a) the materials should be easily generated in a "reasonable" time and b) they should maintain their adsorption capacity over time. One example is shown in Figure 4 for dry $CO_2$ sorption cycling on LDO which is easily regenerated by thermal treatment, though a large drop of $CO_2$ sorption occured after the first cycle. This is attributed to chemisorption of $CO_2$ molecules on to high strength basic sites of LDO. In addition, and as expected, in the absence of impurities, 13X and CaCHA zeolites exhibited stable cyclic capacity over the temperature range investigated. Adsorption/desorption of $CO_2$ was found to be rapid (on the order of seconds). However, in the presence of moisture, $H_2S$ or $NH_3$ the $CO_2$ capacity is substantially diminished. Hence the practical application of these materials to an IGCC process will require pre-treatment of the syngas to remove the impurities, or use of a multi-layered bed in which an appropriate pre-layer is inserted to accommodate the impurities. The low pressure used for regeneration in a pressure swing cycle may also be need to be considered before using these materials. Due to the shape of the isotherm (Figure 1) it may be necessary to augment the low pressure by addition of vacuum pumps.

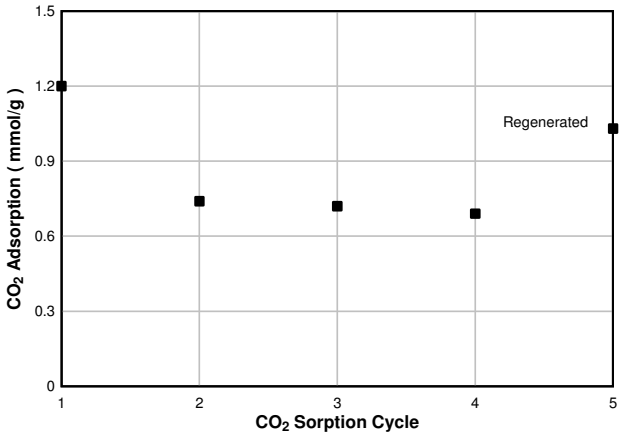


Figure 4 $CO_2$ cycling and regeneration of LDO materials.

Our (and others) cycling experiments on HTC materials suggest they perform very well in the temperature range 300 – 400°C, however, significant chemisorption and reduction in capacity over time is observed. Furthermore the isotherms are non linear so either deep vacuum or extensive purge is required for regeneration. Also there has been significant debate in the literature regarding the kinetics of HTC materials [12]. This may limit the potential usefulness of these materials if the kinetics of desorption are slow as is suggested by some work... However one the few published comparisons between HTC and double salt materials indicates that the kinetics of desorption for the double salt are approximately five times faster than the K promoted HTC [7]. In addition, Na and K-Mg double salts show a very high cycling $CO_2$ capacity in a very narrow temperature range (375 - 400°C) indicating significant PSA cyclic potential. However strong adsorption of $H_2S$ will require protection or thermal regeneration. It is also not currently known what the effect is of water on the $CO_2$ capacity of double salt materials.

## 3. Conclusions

An appropriate adsorbent material for capture of $CO_2$ within an IGCC process requires a range of properties to be satisfied. It is likely that no one material will satisfy all properties and hence the process configurations will need to accommodate weakness of the materials. Of the requirements, $CO_2$ cyclic capacity and tolerance to water and impurities are the most important and will influence the temperature range and regeneration strategy employed. In

this study we presented some of our work on these requirements. On going work is currently being done to validate and test additional materials.

Having screened a number of potential materials, it is possible to devise some process configurations suitable for integration within an IGCC /process. Three possibilities are given below

- 13X retains effective adsorptive properties up to 200°C. However water loading is also significant at this temperature. One possible process option is a prelayer of 13 X for water and $H_2S$ removal at 200°C, followed by a bed of 13 X or CaCHA for carbon dioxide capture.
- HTC (as much recent work indicates) can be an effective adsorbent for carbon dioxide capture at elevated temperatures (350°C) without the requirement of water removal and is a potential candidate adsorbent within a PSA or TSA process. However $H_2S$ loading points to a potential problem. A process including a sacrificial layer for removal of $H_2S$ may be required. In addition, uncertainty regarding the kinetics of adsorption/desorption must be resolved if this adsorbent is to be used. Very slow kinetics will result in long cycle times and large adsorbent beds.
- The double salt adsorbents represents the most promising process options, however the effect of water on the capacity of these materials remains to be determined. Should this effect be detrimental to the performance of the process, it will be necessary to remove the water (possibly using 13X) followed by a TSA process with double salt materials between 375-400°C. Interestingly this TSA cycle offers the opportunity for high pressure capture of the desorbed carbon dioxide.

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